

COLLOIDAL NATURES OF TWO TYPICAL CHINESE VACUUM RESIDUA II: REVISIT AND CHARACTERIZATION OF COLLOIDAL STRUCTURES

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ABSTRACT: Evidences both from TEM observation of Daqing and Shengli vacuum residue and their DOAs prepared by ultra-microtomy and from environmental SEM observation of the untreated Daqing and Shengli vacuum residue and their de-oil asphaltenes confirmed that all of them are of colloidal configurations. It has been generally concluded that, of the microscopic observation tools and the sample treatment techniques employed in the current study of the physical structures of VR, the freezing fracture replication TEM is the best approach in terms of its efficaciousness of displaying the fundamental features of colloidal VR. The independent and combinatorial distribution characteristics of the resins and the asphaltenes are the pivotal parameters in determining the general colloidal features of VR and their de-oil asphaltenes.

KEYWORDS: colloidal structures, vacuum residua, SFEF fractions, SARA fractions

INTRODUCTION

Identification of the colloidal structures of vacuum residua (VR) and their solubility classes is just one aspect concerned by the *Petroleum Physics* studies^[1]. As well documented in previous reports and in the first part of this article^[2,3], the combined SFEF-FFRTEM technique is a sound way in the revelation and characterization of the physical structures of VR on the colloidal scale. For better recognition of the technique, further proofs are strongly required from cross validation experiments in which factors affecting the colloidal structure identification could be manipulated. Among those contributing much to the physical structures of VR, the influence of temperature of the bulk VR on their physical structures accounts for the most besides chemical compositions.

In the procedure of the FFRTEM technique, one issue at point is that the observed samples are to be prepared by freezing replication: the sample is firstly frozen in the liquid nitrogen of -196°C and then replication of the fractured cross-sections of the samples by carbon-coating is conducted in the environment of ca.-120°C. The doubt is that such a process might bring some unrecoverable changes to the physical structures of the bulk VR, which finally results in false deductions about the features and properties of the physical structures of VR. TEM observation of very thin VR samples prepared by ultra-microtomy minimizes the thermal effects on the physical structures of VR. However, it is not clear enough whether the solidification of VR by the solidifying agents in the technique will exert any influences upon their physical structures.

All in all, the VR have to go through a long procedure of physical and/or chemical treatments before they could finally be observed under TEM whether they are prepared by the freezing fracture replication or the ultra-microtomy. In order to take the real images of the untreated VR, Environmental Scanning Electronic Microscopy (ESEM) was attempted to unfold in different manners the physical structures of VR and their formation in terms of solubility classes.

In this part of the paper, not only TEM observations of samples prepared by ultra-microtomy but also their ESEM observations without any physical or chemical treatments were conducted so as to derive more direct evidences, and to lend support to the construction details of the colloidal VR. For deeper understanding of the colloidal VR structures, an attempt will be made to correlate their colloidal features, such as colloidal types and attributes, multidispersity and morphology of dispersed phases, to the SARA pseudo-pure-components.

EXPERIMENTAL

Employment of sample imbedding and ultra-microtomy for TEM observation were made in the present endeavor which serves two purposes: one is to ascertain the comparability of freezing fracture replication in the validity of revelation of the physical structures of VR, and the other is to compare the reliability of different techniques in the reflection of the true physical structures of VR. The introduction of ESEM for the demonstration of the physical structures of VR and their DOAs is another attempt to supply additional proofs to the colloidal identity of VR.

RESULTS AND DISCUSSION

Ultra-microtomy TEM icons of vacuum residua and their SFEF fractions

In Figure 1 is exhibited the TEM photos of Shengli vacuum residua and its DOAs, with the observed samples prepared by ultra-microtomy. As both the solidifying agent and the procedure, such as sample solidifying and the ultra-microtomy, do not interfere with the structural properties of the samples, so the TEM microphotos present images of the vacuum residua and its DOAs without noticeable distortions to the true physical structures.

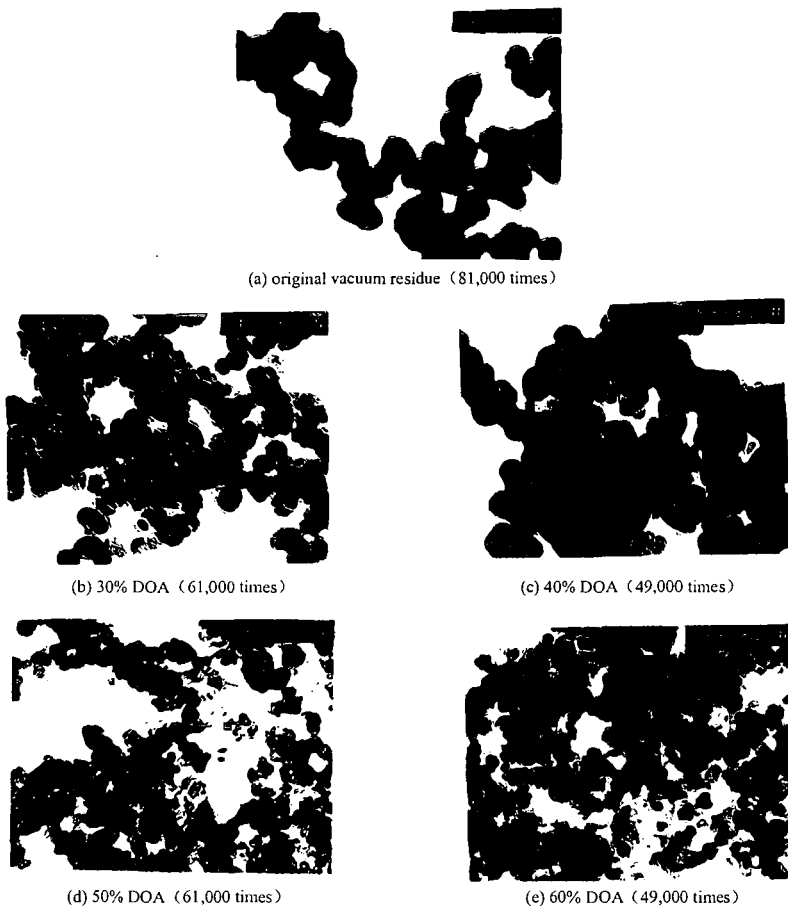


Figure 1 TEM icons of Shengli vacuum residua and its SFEF fractions by ultra-microtomy

It is understandable that, since it is difficult to keep complete consistency of the samples and their viewing areas under microscopes, only the general colloidal features of VR and their DOAs could be compared, such as the morphology of the dispersed phases and the colloidal types. As seen, both the FFRTM photos and the photos in Figure 1 could reflect, in almost the same patterns and similar textures, the colloidal features of the studied vacuum residua and its DOAs.

ESEM icons of vacuum residua and their SFEF fractions

The most useful advantage of ESEM is that not any pretreatment is required for the samples. Thus, it presents true physical structures of samples in a nondestructive manner. However, the ESEM images are not demonstrating the structure details of the bulk phase of samples.

Figure 2 exhibits the ESEM icons of Shengli vacuum residua and its solubility classes. It is obvious that both TEM and SEM can, in combination with appropriate sample preparation procedures, be employed to ascertain and identify the colloidal characteristics of VR and their solubility classes. Therefore it is advisable to select suitable sample preparation techniques and

finer observation tools to compare and contrast the general colloidal features of various VR or their solubility classes. However, it should be reminded that each combination has its own preferable application circumstances. Generally, the FFRTEM technique is the best candidate for studying the physical structures of VR and their solubility classes on the colloidal level while the ESEM technique is preferred when major concerns are about the elemental compositions of the dispersed and dispersing phases. The ultra-microtomy, while useful in exhibiting the colloidal features of VR in combination with common TEM technique, is more appropriate to disclose the pseudo-orderliness of the bulk VR in combination with high resolution TEM technique. Details of the latter two techniques and their usefulness in providing more detailed physical and/or chemical information of the physical structures of VR will be reported later.

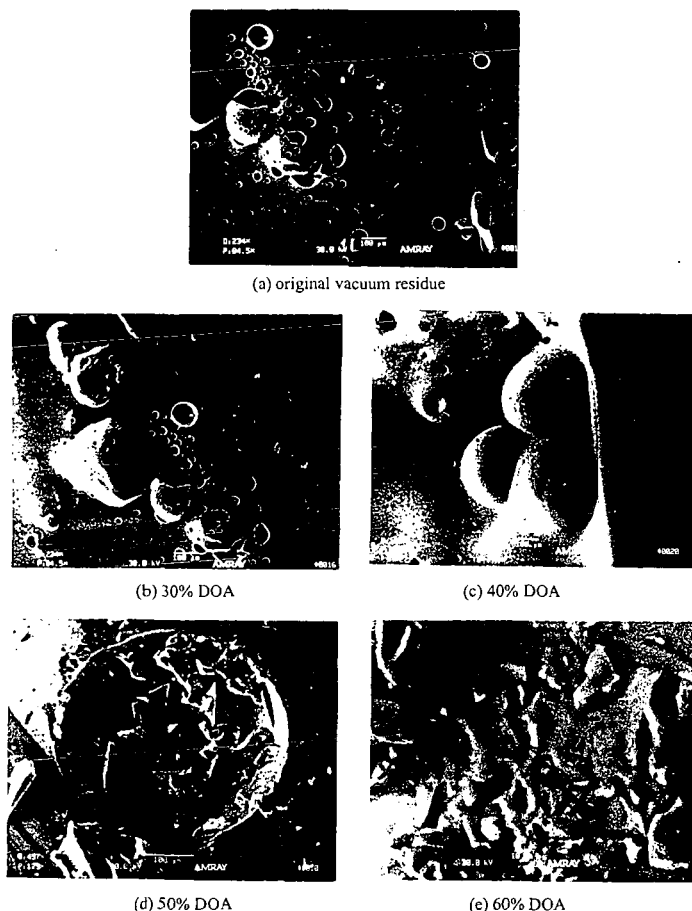


Figure 2 ESEM icons of Shengli vacuum residue and its solubility classes

Characterization of colloidal structures of vacuum residua in terms of SARA compositions

Of all the compositional and structural parameters of VR, their SARA compositions, i.e., saturates, aromatics, resins and asphaltenes, are among the most potential ones capable of characterizing the identity of VR. So it is natural to employ these four pseudo-pure-components of VR to correlate the possible relations which might occur between the general colloidal features of VR and their compositions.

It was confirmed that it was the n-pentane insoluble asphaltenes, which is tantamount to the n-heptane insoluble asphaltenes plus the heavy resins, which construct the micell in the colloidal systems of VR^[5]. Considering the difficulty with which to determine the content of the heavy resins of VR, the content of the total resins is taken, in combination with the content of the asphaltenes (the n-heptane insolubles and toluene solubles), to have an approximate appraisal of the colloidal features of VR and their DOAs, i.e., it is both the asphaltenes and the total resins,

the two kinds of surfactant-like constituents, which are supposed to participate the formation of the micell in the VR. As a matter of fact, since the determination of the SARA compositions of VR has come into the widest use in common petroleum chemistry laboratories, so it is of great significance to employ the SARA compositions of VR to characterize their colloidal structures and general properties. With these in mind, some rough understandings of the relations between the colloidal features of the VR and the quantities of the asphaltenes and/or the resins could be derived by three parameters as defined and specified below.

(1) $W_{Asp} + W_{Re}$: The total amount of asphaltenes and resins is an index which could be used to approximately estimate the quantity of the dispersed phases and their geometrical shapes, as well as their colloidal types. Generally, with the increase of $W_{Asp} + W_{Re}$, more dispersed phases will be formed with their morphologies changing, in the main, from spherical to tabulate, and the bulk structures of the VR and their DOAs transform from sol to sol-gel or gel.

(2) W_{Asp}, W_{Re} : These two independent parameters, in addition to their significance of $W_{Asp} + W_{Re}$, concern the sizes and size distributions of the dispersed phases in VR and their DOAs. Due to the variations in molecular sizes and elemental compositions, the average size of the micell formed by the resins is smaller than that of the micell of the asphaltenes.

(3) W_{Re}/W_{Asp} : The quantity ratio of the resins and the asphaltenes is an indicator for rough evaluation of the aggregation states of the dispersed phases. As the micell of the resins are looser and the micell of the asphaltenes are tighter in terms of the compactness of their molecularly aggregated configurations, so the lower the W_{Re}/W_{Asp} , the tighter the mixed resin-asphaltene micell, which leads to the worse compatibility of these micell with the surrounding dispersing media and less stable colloidal VR and their DOAs.

With the three parameters outlined above, the independent and combinatorial distribution characteristics of the resins and the asphaltenes in the VR and their DOAs are plotted, as shown in Figures 3 through 4. It is obvious that, as the VR and their DOAs become heavier and heavier, both the independent parameter (W_{Re}, W_{Asp}) and the combinatorial parameters ($W_{Re} + W_{Asp}, W_{Re}/W_{Asp}$) vary in rather systematic ways: W_{Re}, W_{Asp} and $W_{Re} + W_{Asp}$ increase and W_{Re}/W_{Asp} decreases as the VR and their DOAs go from lighter to heavier. As the colloidal types and stability of VR and their DOAs are of potential significance in industrial practices, it is instructive to have knowledge of the colloidal types and stability of VR and their DOAs in terms of the independent and combinatorial parameters based on the SARA compositions.

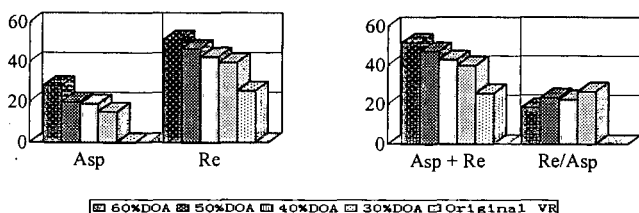


Figure 3 Independent and combinatorial distributions of resins and asphaltenes of Daqing vacuum residue (Data of the asphaltenes in the first graph are plotted in 100 times of their true values, while data of the Re/Asp in the second graph at a tenth of their true values)

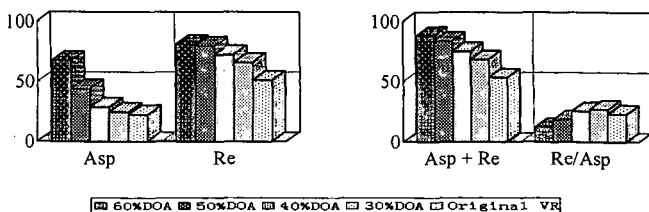


Figure 4 Independent and combinatorial distributions of resins and asphaltenes of Shengli vacuum residue (Data of the asphaltenes in the first graph are plotted in 10 times of their true values)

(1) With the VR and their DOAs becoming heavier, their W_{Re}, W_{Asp} and $W_{Re} + W_{Asp}$ all keep increasing. As both the resins and the asphaltenes are of the characters of surface active molecules, so the average size of the dispersed phases in the VR and their DOAs becomes larger and their quantity becomes more as the VR and their DOAs goes from lighter to heavier. Roughly, for Daqing vacuum residue and its DOAs, the colloidal systems with $W_{Re} + W_{Asp} < 40\%$

are in sol states and the colloidal systems with $W_{\text{Re}} + W_{\text{Asp}} > 50\%$ are in gel states, while for the colloidal systems with $W_{\text{Re}} + W_{\text{Asp}}$ going in-between, they are of the sol-gel states. For Shengli vacuum residue and its DOAs, the approximate values of $W_{\text{Re}} + W_{\text{Asp}}$ corresponding respectively to the sol, sol-gel and gel state are less than 60%, in the range of 60~70% and higher than 70%. The reason why Daqing vacuum residue and its DOAs become the gel states at lower Asp + Re than its Shengli counterparts could be contributed to the fact that, in Daqing vacuum residue and its DOAs, the micell are mainly composed of the resins and the micell of the resins are of loosely aggregated molecular assemblies. These simple analyses not only corroborate again that the dispersed phases in the VR consist of both the resins and the asphaltenes species but also suggest that the relevance of the colloidal types of VR to their critical values of $W_{\text{Re}} + W_{\text{Asp}}$ may be attributed the molecular properties of the resins and the asphaltenes of the specific vacuum residua. It is evident, therefore, that more precise relationship between the colloidal types of VR and such parameters as W_{Re} , W_{Asp} and $W_{\text{Re}} + W_{\text{Asp}}$ could be well defined if the narrower fractions of VR are employed to conduct their colloidal studies and the heavier resins are quantitated.

It is of industrial implication for the colloidal types of VR to be related to W_{Re} , W_{Asp} and/or $W_{\text{Re}} + W_{\text{Asp}}$. In the thermal or catalytic conversion of vacuum residua, both W_{Asp} and $W_{\text{Re}} + W_{\text{Asp}}$ keep increasing; once they reach some critical values, the reaction system comes into the sol-gel state, signifying that the reaction system arrives at the critical state in which the second liquid phase of condensed asphaltenes is about to occur^[4]. As in the thermal conversion of vacuum residua, the appearance of the second liquid phases is immediately followed by the commencement of coke formation, it is therefore of great industrial significance to predict the induction period of coke formation by the real-time monitoring of the variations of W_{Asp} and $W_{\text{Re}} + W_{\text{Asp}}$ or by the establishment of their dynamic equations.

(2) With the VR and their DOAs becoming heavier, their $W_{\text{Re}} + W_{\text{Asp}}$ continues to decrease and accordingly, their colloidal stability keeps decreasing. Since the sol-gel system corresponds to the critical state between stable and unstable colloidal VR, it is estimated from Figures 3 through 4 that the critical $W_{\text{Re}}/W_{\text{Asp}}$ ratio for keeping stability of colloidal VR is ca. 20~25. Such a fact implies that, for Daqing and Shengli vacuum residue and their DOAs, when the value of $W_{\text{Re}}/W_{\text{Asp}}$ is lower than 20~25, their colloidal systems are thermodynamically unstable while when the value of $W_{\text{Re}}/W_{\text{Asp}}$ is greater than 20~25, they remain stable in the sense of thermodynamics.

CONCLUSIONS

(1) With evidences from the FFRTEM, ultra-microtomy TEM and ESEM techniques, it can be well assumed that both Daqing and Shengli vacuum residue as well as their de-oil asphaltenes are all colloidal systems.

(2) Of the three combination techniques for sample preparation and observation, both the FFRTEM and the ultra-microtomy TEM are suitable to study the colloidal structures of VR and their solubility classes in the qualitative way. And just from the viewpoint of the qualitative study of the colloidal structures of VR and their solubility classes, influences from either the freezing in FFRTEM or the solidification in ultra-microtomy TEM could be neglected to some extent.

(3) The colloidal features of VR and their solubility classes could be well characterized by their compositions of the saturates, the aromatics, the resins and the asphaltenes. Particularly, the contents of the resins and the asphaltenes are the two key parameters in the finer characterization of the important colloidal properties of VR, such as the colloidal types of the bulk VR, the morphology and the size and size distribution of the dispersed phases.

ACKNOWLEDGMENTS

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